# Characterizing Hazardous Waste Constituents: A New Tool


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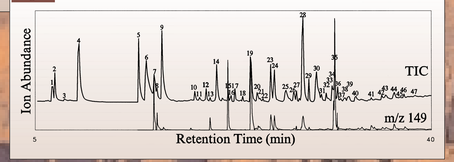
## 1. Problem: Incomplete Characterization of Complex Samples

A typical hazardous waste site accumulates wastes from numerous sources. Over time, these wastes can react to form new compounds, with or without catalysis by solar radiation, components in air, or metals in soil. Hundreds of compounds might be present. To fully characterize each site, every component in numerous samples would have to be identified and quantified. Typically, wastes are analyzed for priority pollutants listed in appendices to EPA methods. In general, these are compounds known to be toxic that are widely used and for which analytical methods exist. These lists represent but a small fraction of the compounds that might be found in hazardous waste sites. New analytical techniques to analyze the other components are needed to assess risks to humans and the ecosystem and are under development at the Environmental Sciences Division of the EPA's National Exposure Research Laboratory.

## 2. Current Practice

Gas chromatography/low resolution mass spectrometry (GC/LRMS) is used to analyze for many of the compounds listed in EPA appendices. When a sample contains dozens of compounds, coelution of multiple components is common, and the mass spectra arise from more than one compound, even after background subtraction. Matches with library mass spectra become poor and compound identification uncertain. This was the case for the extract of a black, viscous sample from a Superfund site in West Virginia; the total ion chromatogram is the upper trace in Figure 1 (1). No credible library matches were found for many mass spectra.

Fig. 1

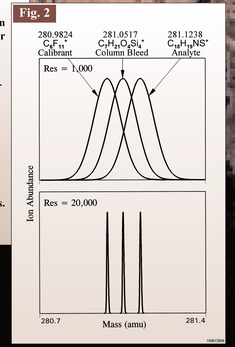



## 3. The Need for High Mass Resolution

High mass resolution is required for two reasons: to separate the signal due to analyte ions from interferences and to provide narrow error limits for exact mass determinations.

Shown in Figure 2 are calculated mass peak profiles at 1,000 and 20,000 resolution for ions produced from the calibrant, from column bleed, and from an analyte, all with a nominal mass of 281 amu. The overlap of the profiles at the lower resolution indicates all three ions would contribute to the signal observed at m/z 281, distorting the mass spectrum and the exact mass obtained for the analyte ion. At the higher resolution, the profiles are baseline resolved and the analyte ion can be monitored without interferences from the other two ions.

Fig. 2




## 4. Additional Information from High Mass Resolution Measurements: Elemental Compositions of Molecular or Fragment Ions

In Table 1 (1) are listed the chromatographic peaks in Figure 1 for the Superfund site sample and the elemental composition for the largest ion containing only the most abundant isotope of each element produced from the compound most responsible for each peak. Only 12 compounds were identified from library matches of mass spectra, and in some cases, the elemental compositions were needed to select the correct match. The identified compounds account for only a small fraction of the total signal and mass of the sample. The $C_8H_7NS^+$ ion (149.0299 amu), indicative of benzothiazole, was measured at a mass resolution of 20,000 (lower trace in Figure 1) and indicated that 11 unidentified compounds contained the benzothiazole group. Benzothiazole derivatives are used in the rubber and dye industries. High resolution data also provided the elemental compositions. Table 1 provides far more information about the sample than could be determined by GC/LRMS alone.

**Table 1. Nominal masses, compositions, and tentative identifications of ions corresponding to chromatographic peaks in the total ion chromatogram**

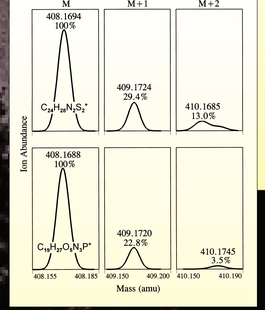
| TIC Peak # | Nominal Mass | Composition | Criteria Met GC | Probe | Tentative Compound Identification |
|---|---|---|---|---|---|
| 1 | 100 | $C_6H_{12}O$ | na | | 2-methyl cyclopentanol |
| 2 | 98 | $C_6H_{10}O$ | na | | |
| 3 | 113 | $C_7H_{15}N$ | na | | n-methyl cyclohexanamine |
| 4 | 93 | $C_6H_7N$ | na | | aniline |
| 5 | 135 | $C_7H_5NS$ | 5 | | benzothiazole |
| 6 | 127 | $C_7H_{13}NO$ | na | | |
| 7 | 149 | $C_8H_7NS$ | 4 | | 2-methyl benzothiazole |
| 8 | 149 | $C_8H_7NS$ | 4 | | 3-methyl-1,2-benzisothiazole |
| 9 | 141 | $C_8H_{15}NO$ | 5 | 2 | |
| 10 | 173 | $C_{12}H_{15}N$ | 5 | | |
| 11 | 178 | $C_{12}H_{18}O$ | 3 | 2 | |
| 12 | 175 | $C_{12}H_{17}N$ | 5 | | |
| 13 | 191 | $C_{11}H_{13}NS$ | 3[a] | | 2-butylbenzothiazole |
| 14 | 169 | $C_{12}H_{11}N$ | 5 | 5 | |
| 15 | 205 | $C_{12}H_{15}NS$ | 5 | 4 | contains benzothiazole group |
| 16 | 192 | $C_{12}H_{16}S$ | 5 | 2 | 1,2,3,4,6,7,8,9-octahydrodibenzothiophene |
| 17 | 187 | $C_{13}H_{17}N$ | 5 | | |
| 18 | 183 | $C_{13}H_{13}N$ | 5 | | |
| 19 | 205 | $C_{12}H_{15}NS$ | 5 | | contains benzothiazole group |
| 20 | 203 | $C_{12}H_{13}NS$ | 2 | | |
| 21 | 219 | $C_{13}H_{17}NS$ | 5 | | contains benzothiazole group |
| 22 | 215 | $C_{13}H_{13}NS$ | 5 | | |
| 23 | 205 | $C_{12}H_{15}NS$ | 5 | | alkylated benzothiazole |
| 24 | 205 | $C_{12}H_{15}NS$ | 5 | | alkylated benzothiazole |
| 25 | 199 | $C_{12}H_9NS$ | 4 | | phenothiazene |
| 26 | 234 | $C_{13}H_{18}N_2S$ | 4 | | |
| 27 | 246 | $C_{14}H_{18}N_2S$ | 5 | 4 | |
| 28 | 232 | $C_{13}H_{16}N_2S$ | 5 | | N-cyclohexyl-2-benzothiazolamine |
| 29 | 246 | $C_{14}H_{18}N_2S$ | 5 | | methyl-N-cyclohexyl-2-benzothiazolamine |
| 30 | 226 | $C_{13}H_{10}N_2S$ | 5 | | o-anilinophenylester thiocyanic acid |
| 31 | 266 | $C_{18}H_{22}N_2$ | 5 | | |
| 32 | 281 | $C_{18}H_{19}NS$ | 5 | | |
| 33 | 260 | $C_{14}H_{16}ON_2S$ | 5 | | |
| 34 | 260 | $C_{18}H_{16}N_2$ | 5 | 3 | |
| 35 | 285 | $C_{18}N_{23}NS$ | 5 | | contains benzothiazole group |
| 36 | 283 | $C_{18}H_{21}NS$ | 4 | | contains benzothiazole group |
| 37 | 280 | $C_{16}H_{28}N_2S$ | 5 | | |
| 38 | 286 | $C_{18}H_{26}ON_2$ | 5 | 3 | |
| 39 | 308 | $C_{19}H_{20}N_2S$ | 5 | | |
| 40 | 268 | $C_{14}H_8N_2S_2$ | 5 | | |
| 41 | 296 | $C_{18}H_{20}N_2S$ | 5 | | |
| 42 | 314 | $C_{19}H_{26}N_2S$ | 5 | | contains benzothiazole group |
| 43 | 290 | $C_{18}H_{14}N_2S$ | 5 | | contains benzothiazole group |
| 44 | 326 | $C_{18}H_{18}N_2S_2$ | 5 | 3[b] | contains benzothiazole group |
| 45 | 354 | $C_{20}H_{22}N_2S_2$ | 5 | | |
| 46 | 372 | $C_{24}H_{24}N_2S$ | 4 | | contains benzothiazole group |
| 47 | 336 | $C_{19}H_{16}N_2S_2$ | 5 | | |
| | 301 | $C_{19}H_{13}N_2S$ | | 3[c] | |
| | 365 | $C_{21}H_{21}N_2S_2$ | | 4[c] | |
| | 402 | $C_{24}H_{22}N_2S_2$ | | 4 | |
| | 408 | $C_{24}H_{28}N_2S_2$ | | 5 | |

[a]Criteria tested for m/z 162 ion due to low signal
[b]Insufficient to exclude all other compositions not containing P atoms
[c]For this ion, an absence of P atoms was assumed

## 5. Using Isotopic Masses and Relative Abundances to Identify Large Ions

The number of elemental compositions possible for an exact mass within the error limits of its determination increases rapidly with the mass of the ion. Only 5 of the ions in Table 1 were identified from the exact mass of the ion containing only the isotopes with greatest natural abundance (M). The other ions were identified using criteria based on the exact masses and relative abundances of ions with masses 1 or 2 amu greater than M, denoted as M+1 and M+2 (2). The mass peak profiles in Figure 3 were calculated for the last ion in Table 1 and for 1 of 17 other compositions possible based on the exact mass determined for M. The differences in the exact mass of the M+2 profile and the abundances of the M+1 and M+2 profiles relative to the M profile were large enough to eliminate the bottom composition. Peak broadening of the upper M+2 profile arises from the mass difference between $C_{24}H_{28}N_2S^{34}S^+$ (410.1652 amu) and $^{13}C_2C_{22}H_{28}N_2S_2^+$ (410.1761 amu). The shape and width of the M+2 profile are also useful for distinguishing between possible compositions.

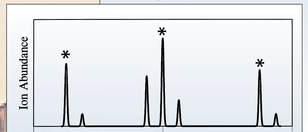
Fig. 3




## 6. The New Analytical Technique that Provides Elemental Compositions

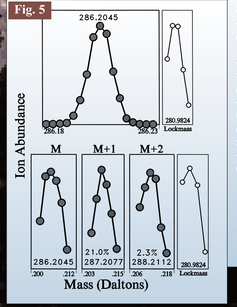
Mass Peak Profiling from Selected Ion Recording Data (MPPSIRD) is a new data acquisition technique that increases sensitivity 100-fold and speed by a factor of 6 over conventional scanning modes at a resolution of 20,000. Full scans at high mass resolution have long been used to determine exact masses of synthetic products introduced into the ion source over an extended period of time, but have not been used to obtain exact masses for ions produced from compounds that enter the source as narrow chromatographic peaks, because the scan rate is too slow to track the peaks and because the sensitivity is too low to observe many components in mixtures. In Figure 4, a full scan is shown. Data are acquired as the m/z ratio observed varies continuously across the entire mass range. With Selected Ion Recording (SIR), a set of individual m/z ratios is monitored to provide much greater sensitivity and speed. SIR has been used historically to monitor m/z ratios atop mass peak profiles resulting from target analytes as illustrated by the asterisks in Figure 4.

Fig. 4




In Figure 5, the new technique is illustrated. To plot the full mass peak profile, m/z ratios were monitored across a single profile (3). To plot the partial profiles, 6 m/z ratios each were monitored across the top portion of the M, M+1, and M+2 profiles (4). Monitoring of partial profiles provides a rapid cycle time (0.8 sec), which enables tracking of chromatographic peaks. The exact mass of a profile is obtained as the weighted average of several m/z ratios taken across the top of the profile. Triplicate exact mass determinations at 20,000 resolution using a mass increment of 5 ppm provided masses accurate to within 2.5 ppm. A Profile Generation Model (2) predicts the exact masses and relative abundances expected for all possible compositions when six m/z ratios are monitored across M, M+1 and M+2 profiles and applies criteria to reject those compositions that are not consistent with the data. Elemental compositions can almost always be determined for ions with masses less than 600 amu and for larger ions in many cases (2).

Fig. 5




## 7. Screening for Target Compounds

The extract was introduced with a heated probe while the M, M+1, and M+2 partial profiles were monitored for each of 9 ions listed in Table 1 that contained different numbers of N, O, or S atoms to learn if their compositions could be determined rapidly without prior component separation (1). All but the correct composition were rejected for 8 of the 9 ions.

A poor library match for strychnine ($C_{21}H_{22}N_2O_2$; 334.1681 amu) was found for a trace component, which was determined to be $C_{24}H_{18}N_2$ (334.1470 amu). When probe introduction was used to screen for strychnine, no signal was observed for the M, M+1, or M+2 ions from strychnine. Thus, to a very low detection limit, strychnine was not found in the extract.

## 8. Other Applications of MPPSIRD

MPPSIRD is used routinely in our laboratory with GC and probe introduction. The last 4 ions in Table 1 were identified using the probe, since chromatographic peaks were not observed for these ions. Quantitative analysis of Aroclors (mixtures of PCBs) using a carbon-labeled PCB isomer as the calibration standard has also been demonstrated (5). Many environmental contaminants are too labile, polar, or large to provide chromatographic peaks. Liquid sample introduction techniques [microscale liquid chromatography (μ-LC), capillary electrophoresis (CE), and capillary electrokinetic chromatography (CEC) coupled to electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) mass spectrometry] are currently being investigated. These techniques employ "soft" ionization and will provide molecular or quasi-molecular ions for most compounds.

## 9. SUMMARY

A new high resolution mass spectrometric technique (MPPSIRD):
- provides elemental compositions for ions with masses up to 600 Da
- helps identify major and trace components in complex mixtures
- quantifies mixture components using an internal standard

Elemental compositions are used to:
- reject library matches with incorrect compositions
- confirm library matches with the correct composition
- limit a compound's identity to a number of isomers

High mass resolution:
- provides high selectivity by separating analyte ion signals from interferences
- permits determination of exact masses within small error limits.

Plotting mass peak profiles from selected ion recording data provides:
- high sensitivity enabling use of 20,000 resolution
- a fast cycle time to track chromatographic peaks
- a highly selective, sensitive, and rapid screening technique for target analytes

## 10. REFERENCES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